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**High Pressure Boron Ignition and Combustion**  
**AASERT Grant Number N00014-93-1-1206**

for the period July 21, 1993 - July 20, 1996

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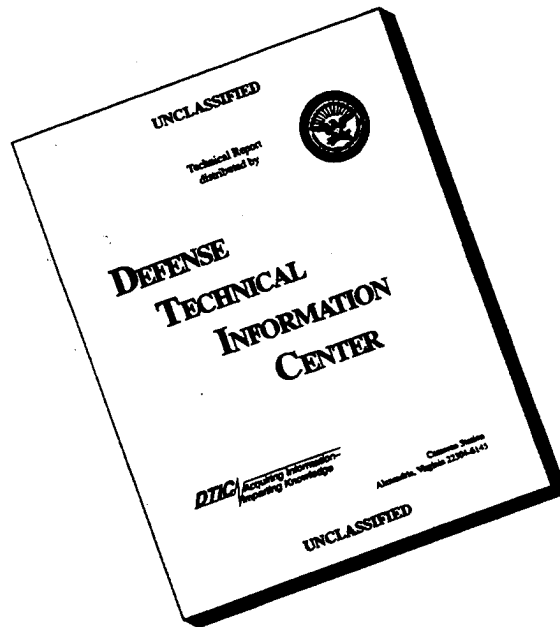
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13. ABSTRACT (Maximum 200 words) The high potential energy release of boron makes it a prime candidate for a high enthalpy fuel or as a fuel additive to solid propellant formulations, as well as a prospective additive for tailoring energy release rates of explosive grains. The problem of long ignition delays at atmospheric and lower pressures, caused by a combination of factors which include the necessity to remove a combustion-retarding oxide layer from the particles, a high vaporization temperature for the pure boron substrate, and slow condensation kinetics, have generally precluded the use of boron for energetic fuel applications at these pressures. This report summarizes experiments which measure an order of magnitude shorter ignition delays than previously published 1 atm data, for pure and reduced oxygen and oxygen mixtures with water vapor and fluorine compounds (H <sub>2</sub> , HF) over 8.5 to 34 atm and 2000 to 3000 K. Ignition delays in the 300 to 500 microsecond range are observed in a shock tube, decreasing with increasing temperature, and increasing two-fold when oxygen concentrations are reduced to 5% in Ar. Fluorine, from dissociated 1% SF <sub>6</sub> in O <sub>2</sub> , is seen to decrease ignition delays by a factor of 1.7 compared to pure oxygen. A combustion chamber is used at a peak pressure of 157 atm and temperature in excess of 2800 K to study ignition delays at higher pressures than are possible in the shock tube. Endwall emission spectra of BO <sub>2</sub> are recorded for comparison with boron ignition models.					
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## SECTION I

### REPORT OVERVIEW -- Part 1

#### IGNITION AND COMBUSTION OF BORON PARTICLES IN HYDROGEN/OXYGEN EXPLOSION PRODUCTS

The high potential energy release of boron makes it a prime candidate for a high enthalpy fuel or a fuel additive to solid propellant formulations as well as a prospective additive for tailoring energy release rates of explosive grains. The problem of long ignition delays at atmospheric and lower pressures, caused by a combination of factors which include the necessity to remove a combustion-retarding oxide layer from the particles, a high vaporization temperature for the pure boron substrate, and slow condensation kinetics, have generally precluded the use of boron for energetic fuels applications at these pressures. Until recently very little was known about the ignition and burn behavior of boron particles at higher pressures and temperatures, and this newer work indicates that operation at higher pressure may significantly reduce the ignition delays.

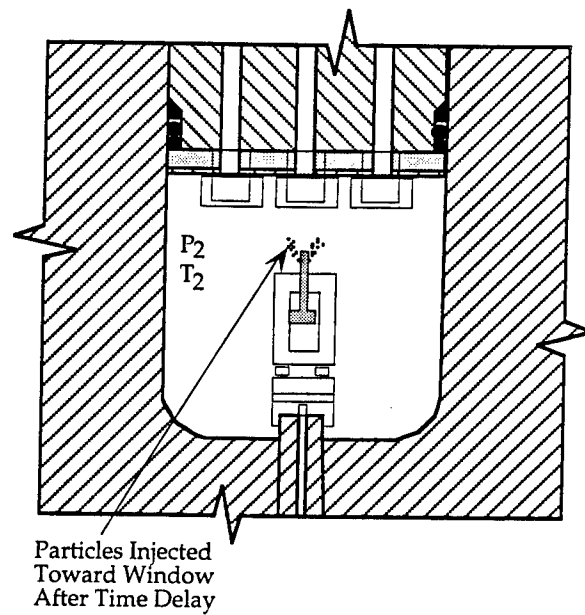
Much of the previous research involving either laser initiation or atmospheric and sub-atmospheric pressure burning in flames has indicated fairly lengthy ignition delay times on the order of 2 to 10 milliseconds [1,2] for particles of mean diameter of 34 to 44  $\mu\text{m}$ , and between 1 and 10 milliseconds for particles of 7 to 10  $\mu\text{m}$  size in wet flames. More recently we have published results from our own experiments which measured an order of magnitude shorter ignition delays in pure and reduced oxygen and in oxygen mixtures with water vapor and fluorine compounds (F, HF) over 8.5 to 34 atm and 2000 to 3000 K [3, 4]. It was demonstrated that ignition delays were in the 500 to 300  $\mu\text{sec}$  range, decreasing with increasing temperature, and increased 2-fold when oxygen concentrations were reduced to 5% in Ar. Fluorine, from dissociated 1%  $\text{SF}_6$  in  $\text{O}_2$ , was seen to decrease ignition delays by a factor of  $\sim 1.7$  compared to pure oxygen over the temperature range studied.

Limited results have been available to date for boron particle ignition at higher pressures ( $\sim 52$  atm) because we have found the ignition delay time of  $\sim 24$   $\mu\text{m}$  crystalline boron to be on the order of 100 to 400  $\mu\text{sec}$ , times shorter than the characteristic temperature and pressure establishment times in our high pressure combustion chamber[4]. Tests are conducted in a high pressure, constant volume combustion bomb apparatus which has been fabricated and instrumented for this study [4] (see Fig. 1). The combustion chamber consists of a 1000 kg main

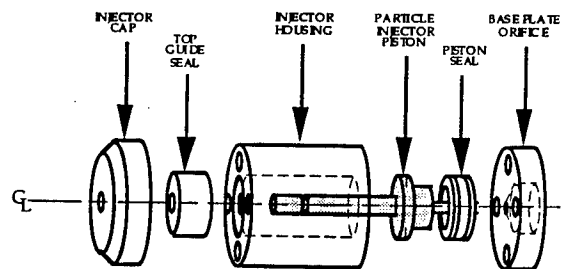
vessel which holds a 2.0 liter, 14.2 cm diameter cylindrical chamber cavity. The device is instrumented for measurements of pressure, ignition signal, and spectral signal acquisition, and has been designed for transient combustion tests up to 3400 atm. To alleviate the problem of early particle ignition, we have designed a novel particle injection device shown in Fig. 2 which keeps the particles unexposed from the combusting ambient gases long enough for quasi-equilibrium conditions to be established. The pressure rise from the combusting ambient gases is used to inject the particles after sufficient delay and the injection has been actively timed and found to be very repeatable.

In this paper we report on newer findings on the ignition and combustion behavior of crystalline boron particles at high pressures ( $\sim 80$  and  $160$  atm) and temperatures ( $2400 - 2870$  K). Particles of nominal size  $24$ ,  $34$ , and  $50\ \mu\text{m}$  are ignited and combusted in the products of nitrogen diluted hydrogen/oxygen explosions and a few tests with  $\text{CO}_2$  additive to simulate hydrocarbon combustion products. The effects of the ignition-enhancing agents water vapor,  $\text{CO}_2/\text{CO}$ , and  $\text{NO}$  on ignition and burn characteristics of particulate boron at high pressures are reported for the first time. Time resolved, band-pass filtered boron particle emissions are measured at selected wavelengths to give optimal differentiation between particle laden and no-particle background signals which are not negligible at these pressures. Spectrometric measurements have shown filtering at  $545$  and  $514\ \text{nm}$  (which correspond to two well-known gaseous  $\text{BO}_2$  molecular bands, where  $\text{BO}_2$  is a transient intermediary species) to be optimum at our conditions.

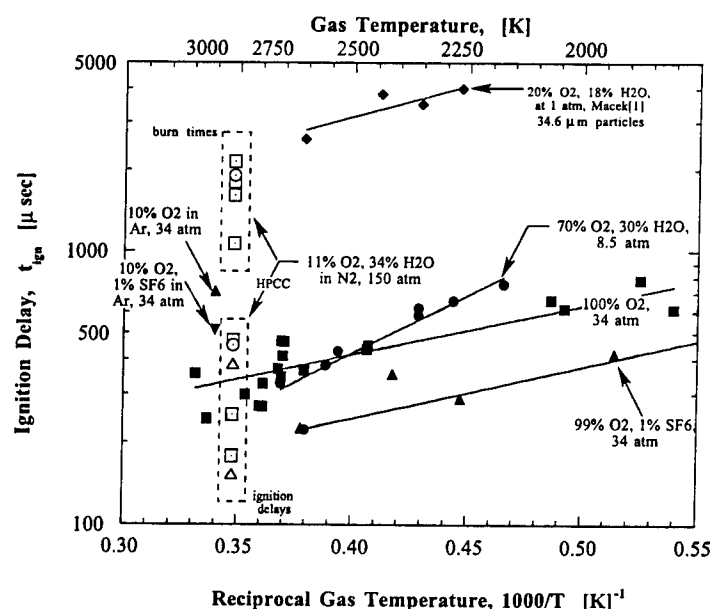
Preliminary test results for ignition delay and burn times of  $24\ \mu\text{m}$  crystalline boron are shown in Fig. 3 for the nominal test mixture consisting of  $2\ \text{H}_2 + 1.7\ \text{O}_2 + 3\ \text{N}_2$ , which yields  $10\%$   $\text{O}_2$  and  $34\%$   $\text{H}_2\text{O}$  final composition at  $2870\ \text{K}$ , based on equilibrium calculations. The ignition delays at  $150\ \text{atm}$  in nitrogen diluted oxygen/water vapor are just slightly shorter than comparable  $34\ \text{atm}$  data, but an order of magnitude shorter than  $1\ \text{atm}$  delays measured by Macek[1]. Previous data[4] show that fluorine compounds reduce ignition delays at  $34\ \text{atm}$  and the pressure effects of this enhancement will be studied further in the combustion chamber. Analysis of pressure effects, nitrogen dilution, post gas-explosion oxygen concentration, and particle size will be included.



**Fig. 1 :** Chamber section of high pressure combustion chamber (hpcc) apparatus for particle ignition and combustion studies (3400 atm design pressure). Shows particle injector location.



**Fig. 2 :** Schematic of particle injector which provides repeatable injection after sufficient delay for gas combustion to equilibrate in chamber.



**Fig. 3 :** Plot of crystalline boron particle ( $\sim 24 \mu\text{m}$ ) ignition delay times in products of nitrogen diluted hydrogen/oxygen explosions. Reduced oxygen data with ignition enhancers at lower pressures are shown for comparison.

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## REPORT OVERVIEW -- Part 2

### Time-Resolved Emission Spectroscopy of Burning Boron Particles at High Pressures

The ignition and combustion of boron particles is the subject of considerable research. Much data exists on the ignition delay and burn time characteristics of boron particles in various oxidizers [1,2,3]. Work has also been done to obtain spectroscopic data from burning particles [3,4]. Most of this work, however, has been done at atmospheric pressure. This paper will outline tests being done on boron ignition and combustion in various oxidizers at pressures ranging from 8.5 to 34 atm. Ignition delay data and time-resolved emission spectra are recorded and the results are compared with models of boron particle ignition.

The data presented here was collected in the shock tube high-pressure combustion apparatus at the University of Illinois. Boron particles are ignited in the region behind a reflected shock wave at the endwall of the shock tube. The endwall is equipped with a quartz/lexan composite window which allows light emitted by the burning particles to be collected and focused onto photodiodes and a spectrometer. Specific information on operation of the shock tube is presented elsewhere [5]. The spectral data is collected using an EG&G 1460 Vidicon Optical Multi-Channel Analyzer, a 1254 Detector, and a model 1211 pulse generator. The pulse generator enables the recording of single snapshots of spectra with pre-set exposure and delay times. Typical exposure times in these experiments were 50, 100, 250, and 999  $\mu\text{s}$  with delay times of 0, 250, or 2000  $\mu\text{s}$  between shock arrival at the endwall and beginning of exposure.

Ignition delay studies have been performed for boron particles of various sizes in atmospheres of pure  $\text{O}_2$  and in  $\text{O}_2$  atmospheres containing the ignition-enhancing additives  $\text{SF}_6$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$  [5]. Figure 1 shows the ignition delay time versus temperature for 24  $\mu\text{m}$  boron particles in pure  $\text{O}_2$  and in a mixture of 1%  $\text{SF}_6$  and 99%  $\text{O}_2$  at a pressure of 34 atm. It is apparent that the ignition delay time is decreased with the addition of  $\text{SF}_6$ . This trend is in agreement with theory and experiments presented by other researchers [6].

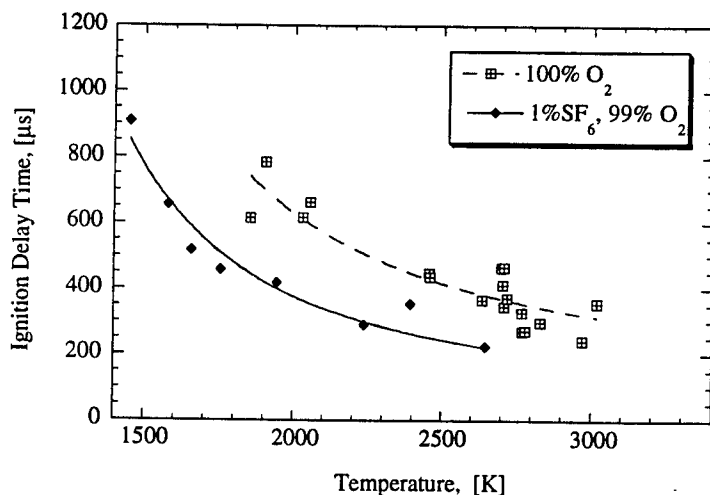


Figure 1. Ignition delay time versus temperature of the third peak comparing  $\text{SF}_6$  and  $\text{O}_2$  for 24  $\mu\text{m}$  boron particles at 34 atm.

however, the  $\text{SF}_6$  spectra shows a shift to higher energies compared to the pure  $\text{O}_2$  spectra. This result agrees with theory in that the reaction of boron with  $\text{SF}_6$  is more vigorous than with pure  $\text{O}_2$ .

Emission spectra of light emitted from burning boron particles in pure  $\text{O}_2$  and  $\text{O}_2/\text{SF}_6$  atmospheres have been recorded at various times during the combustion process. Figure 2 shows two spectra, one taken during a shot with  $\text{SF}_6$  additive at 8.5 atm and 2600 K. The second spectra is that taken during a shot with pure  $\text{O}_2$  at the same temperature and pressure. The exposure time was 250  $\mu\text{s}$  and the delay between shock arrival and exposure was set to 250  $\mu\text{s}$  for both spectra. Both spectra show characteristic  $\text{BO}_2$  emission bands [3,4,7],

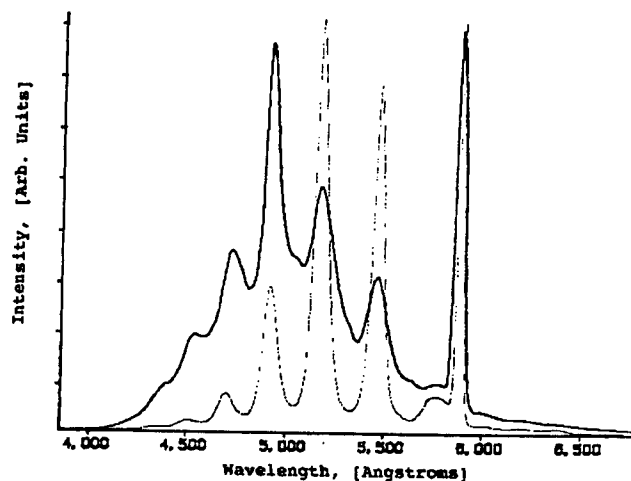


Figure 2.  $\text{BO}_2$  spectra from boron combustion at 8.5 atm. and 2600 K in an atmosphere of 1%  $\text{SF}_6$  with 99%  $\text{O}_2$ . The spectra from a shot in pure  $\text{O}_2$  at the same temperature and pressure is shown for comparison.

Other experiments performed using  $\text{H}_2\text{O}$ ,  $\text{NO}$ , and  $\text{CO}_2$  as additives are used to give quantitative and qualitative comparisons to combustion theories and models. Spectral data is also used to determine reaction rate constants at high temperature and pressure, which is required for the validation of computer models of boron combustion.

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## SECTION II

### SHOCK INITIATION OF CRYSTALLINE BORON IN OXYGEN AND FLUORINE COMPOUNDS

Herman Krier,<sup>\*</sup> R. L. Burton,<sup>†</sup> S. R. Pirman,<sup>‡</sup> and M. J. Spalding<sup>‡</sup>

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#### ABSTRACT

The ignition delay and combustion of amorphous and crystalline boron particles is investigated at elevated temperatures and pressures for wet, dry, and fluorine-containing atmospheres. Micron-sized amorphous and sieved 20  $\mu\text{m}$  crystalline particles are ignited in the reflected-shock ambient conditions produced at a shock tube endwall. The ignition delay and combustion times are examined as a function of temperature for pressures of 8.5, 17, and 34 atm. and for oxidizer mixtures of 100% oxygen, 30% water vapor, 1-3% sulfur hexafluoride, and 6-12% hydrogen fluoride. At 8.5 atm.  $\text{SF}_6$  has little effect on the ignition delay or temperature limit for 20  $\mu\text{m}$  particles, but at 34 atm. the effect of  $\text{SF}_6$  is to reduce both the ignition delay time and the ignition temperature limit, from 1900 K to 1400 K. In addition, experiments conducted with 1  $\mu\text{m}$  and 20  $\mu\text{m}$  crystalline boron particles and with  $<200 \mu\text{m}$   $\text{B}_2\text{O}_3$  particles show that the first and second peaks observed in 20  $\mu\text{m}$  particle combustion are associated with removal of the oxide layer.

#### INTRODUCTION

The potential of high energy density materials to achieve a controlled high energy release has instigated extensive research on liquid and solid propellant combustion applications. Whether the energetic material is used for rocket propulsion or detonation purposes, performance increases are always a major goal. A concentrated effort has also been placed on studying metallized solid propellant combustion, which can yield large amounts of energy per unit volume. Currently,

aluminum and magnesium are the metals of choice, although boron produces an even higher energy release. In this paper research is presented on boron combustion with various oxidizers at high pressures [1].

### **Benefits of Boron as a Fuel**

Boron has great potential for use as an additive energetic material. Apart from being a relatively common element, it has the greatest heating value of any fuel except beryllium, which reacts with oxygen to form extremely toxic BeO. Boron can also be used for controlled, non-ideal detonations. Its high energy output coupled with a delayed reaction generates an increased pressure-volume process, which results in more work output.

### **Disadvantages of Boron as a Fuel**

For a material to be a viable candidate for a fuel or fuel additive, it must be able to ignite, burn, and release its energy within the combustor region of a rocket motor. Unfortunately, the ignition delay and combustion times for boron may not meet this criterion for most applications [2]. The main reason that boron is difficult to ignite is that the particle is coated with an oxide layer of  $B_2O_3$ .

The  $B_2O_3$  layer, present whenever the particle is in an oxygen-containing atmosphere, inhibits further oxidation of the particle and therefore restricts the ignition process. Above a particle temperature of 723 K, the oxide layer liquefies. This allows some oxygen to diffuse slowly through the liquid layer and react with the boron. However, the reaction then produces more oxide and increases the thickness of the oxide layer, which retards the diffusion process as well as the combustion of the particle.

In addition, full utilization of energy from the combustion reaction is difficult to achieve because a significant fraction of the energy is never released. Because boron has high melting and boiling temperatures, the heating of the particle can continue for a time longer than the residence time in a combustor. If the particle happens to react completely, most of the products formed will be in the gas phase. Highest energy output is not achieved until the products condense to liquid

phase. Since the boron product condensation process is relatively slow until the temperature drops significantly, the benefits of product condensation are usually never realized [2, 4]. The trapping of the products in the gas phase can potentially reduce the heating value of boron by up to 25 percent.

### **Comparison of Boron with Aluminum**

Other solid fuels have qualities similar to boron, so that it would seem that the combustion process might also be similar. For instance aluminum, which is in the same group on the periodic table as boron and has been utilized extensively for rocket propulsion, also forms an oxide layer upon heating, which is similar to the structure of boron oxide ( $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ ). Table I lists some of the properties of boron and aluminum and their oxides. However, the two elements and their oxides display significantly different melting and boiling temperatures and enthalpy of fusion (Table I). There is consequently little in common in their ignition processes [2, 5].

The ignition and combustion of aluminum has been studied extensively by many researchers, including Roberts, et al. [5, 6], who conducted their shock tube experiments with a similar configuration used for the present boron research. For aluminum, an oxide layer forms during heating in an oxygen-containing atmosphere. Before the aluminum melting point is reached, the aluminum expands and the oxide layer breaks apart allowing oxygen to reach the aluminum particle [5]. As the particle temperature increases to the melting point of the oxide, the oxide layer retracts to expose the bare particle, and allows a vigorous ignition reaction between the liquid aluminum particle and the oxidizer. The liquid droplet has a detached gas phase envelope where homogeneous combustion of the particle occurs. To complete the process, the product  $\text{Al}_2\text{O}_3$  condenses out, releasing the additional enthalpy of vaporization.

Boron particle ignition follows a completely different process. After initial particle heat-up, the oxide layer melts long before the boron particle melts (Table I). This allows the oxidizer to diffuse through the oxide layer and react with the particle, starting the ignition process. The oxide layer then builds up, retarding further oxidation. As the particle temperature increases further, the oxide

**Table I.** Physical properties of amorphous (Am.) and crystalline (Cr.) boron, aluminum, and their oxides,  $B_2O_3$  and  $Al_2O_3$ .

Physical Property	B-Am.	B-Cr.	$B_2O_3$	Al	$Al_2O_3$
$\rho$ [kg/m <sup>3</sup> ]	2220 [3]	2350 [7]	2990 [12]	2700 [8]	3980 [8]
$\kappa$ [W/m K] at 300 K	27.6 [10]	27.4 [7]	---	237 [8]	36 [8]
$\kappa$ [W/m K] at 800 K	8.1 [10]	7.36 [12]	---	218 [8]	10.4 [8]
$c_p$ [J/kgK] at 300 K	1116 [12]	1055 [9]	1026 [7]	903 [8]	765 [8]
$c_p$ [J/kgK] at 800 K	---	2144 [12]	1863 <sup>a</sup> [9]	1146 [8]	1180 [8]
$T_{mp}$ [K]	---	2350 [9]	723 [7,9]	933 [12]	2327 [12]
$T_{bp}$ [K]	---	4138 [9]	2316 [9,11]	2791 [12]	3253 [12]
$T_{ign}$ [K]	1073 [13]	1950 [11]	---	2327 [5]	---
$H_{fus}$ [kJ/mol]	---	50.2±1.7 [9]	24.1±0.4 [9]	10.7±0.2 [9]	111±4 [9]
$H_{vap}$ [kJ/mol]	---	480 [9]	---	294 [9]	---
$MW$ [kg/kmol]	10.81 [12]	10.81 [12]	53.62 [12]	26.98 [12]	101.96 [12]

<sup>a</sup> - at 723 K

begins to evaporate, removing energy from the particle. At a certain point the energy released from the chemical reaction exceeds the energy absorbed from evaporation and heat loss, and the remaining oxide suddenly evaporates. The particle then re-ignites and heterogeneously combusts. It is difficult to achieve homogeneous gas phase combustion of the boron particle because the boron boiling point is relatively high (Table I), so that the combustion reaction consists mainly of surface reactions. Because the product  $B_2O_3$  remains in the gas phase, the benefits of energy release from condensation are lost in rocket motor applications.

## Research Background

Because the benefits of boron-based combustion are apparent, research continues on how to exploit its advantages. There are numerous experiments reported which study the ignition process and attempt to establish a starting database for boron ignition and combustion models.

In 1982, King [2] reviewed several models and described the basic boron particle combustion process. Figure 1 shows a diagram of boron particle processes during heating [14]. It has been theorized [15] that the intermediate species BO and BO<sub>2</sub> are slow to react to form B<sub>2</sub>O<sub>3</sub>, resulting in the long ignition delays observed in the experiment. Others have hypothesized that those species are not intermediate, but are final products. Yeh and Kuo state that the rate-limiting step is the combination of gaseous O<sub>2</sub> with a (BO)<sub>n</sub> polymer to form gaseous BO<sub>2</sub> and adsorbed oxygen [14]. The general consensus is that faster removal of the oxide layer will decrease ignition delay times.

Experimental evidence has shown a reduction in ignition delay in atmospheres containing water vapor [16, 17]. Other experiments have shown a reduction in ignition delay for atmospheres containing other compounds, such as species containing fluorine [18]. These chemical reactions release gaseous products such as HBO<sub>2</sub> or possibly OBF. However, these models are difficult to evaluate because there is little supporting experimental data.

The present study expands the boron ignition database to include the ignition of boron particles in oxygen at pressures ranging from 8.5 to 34 atmospheres, and in gases containing SF<sub>6</sub>/O<sub>2</sub> and HF/O<sub>2</sub> mixtures. The first compound is utilized to study the effect on boron ignition of fluorine atoms, which may increase the energy output of boron combustion as well as reduce its ignition delay. Sulfur hexafluoride dissociates easily at relatively low temperatures (< 2000 K), providing an excellent source of fluorine atoms. Hydrogen fluoride does not dissociate easily, so the complete molecule must interact with the boron particle. It has been proposed that the HF molecule will reduce the particle ignition delay even further [19].

## EXPERIMENTAL TECHNIQUE

The experiments consisted of igniting and combusting 1-50 μm boron particles with various oxidizers at the endwall of a 12 m shock tube [1,5,20]. The endwall region is well suited for particle combustion studies since the flow velocity is nearly zero. The main limitation of this technique is the short duration of the test conditions, due to the arrival of pressure disturbances

from the interaction of the reflected shock wave and the flow contact surface. In these experiments, the pressure disturbances do not arrive until after the ignition event has ended.

To create the desired conditions, the shock tube driver section is filled with high pressure gas (condition 4), and the 8.9 cm diameter driven section with a low pressure gas (condition 1). All conditions are depicted in Fig. 2. Details of the gas dynamics equations utilized to solve for  $P_5$  and  $T_5$  for a given  $P_4/P_1$  are presented elsewhere [5,6].

### Experimental Procedure

The 8.4 m long driven section is coupled to a 3.3 m long, 16.5 cm diameter stainless steel driver section by a converging nozzle/dual-diaphragm section with Mylar diaphragms. A reduced diameter driven section provides an efficient steady expansion and also reduces the driver pressure necessary to produce given test conditions, compared to a constant area shock tube [21].

The boron particles are held with a small amount of finger oil on a hobby knife blade mounted 8 mm from the endwall (Fig. 3). The endwall houses a quartz/polycarbonate composite window which allows emitted radiation to be monitored with a photodiode mounted outside of the shock tube. The particles are blown off the knife blade toward the endwall by the high velocity flow behind the incident shock wave. After the reflected shock passes, the particles drift in the stagnant gas and collide with and reflect off the endwall. The particles are then ignited (Fig. 3) and are sufficiently dispersed that the radiation from a hot particle does not contribute to the heating of adjacent particles, making the experimental results independent of the number of combusting particles [5,6].

Various procedures are followed for filling the driven section, depending on the oxidizer [1]. Oxygen is admitted as a gas. Water vapor and  $\text{SF}_6$  are admitted by evaporation of the liquid phase. Hydrogen fluoride requires special precautions. Because it is a corrosive gas, the HF bottle is stored in a fume hood. An NaOH scrubber is used to neutralize combustion products before being discharged to the atmosphere. A dry nitrogen flushing system drives the hydrogen fluoride out of



the shock tube, which is made HF-resistant with Teflon seals. The HF etches the quartz window, which is replaced when corrosion becomes excessive.

For HF, the tube is first filled with nitrogen to approximately 650 kPa. This step allows for the detection of leaks and purges moisture from the system when the nitrogen is vented off. After filling to the desired partial pressure of oxygen, hydrogen fluoride is introduced into the tube with a fast-acting solenoid and an air-lock valve arrangement, which prevents large amounts of evaporating liquid HF from entering. After the hydrogen fluoride is injected, it reacts with the wall and "plates" out, reducing the pressure. The injection procedure is repeated until no pressure drop is observed in the driven section.

### **Experimental Data**

The data required from the shock tube are the conditions of the gas behind the reflected shock and the time it takes the boron to ignite and burn. The temperature and pressure are calculated from the initial driver conditions and the velocity of the incident shock wave, measured with piezoelectric pressure transducers located on the sidewall and endwall of the shock tube, and recorded on a Soltec ADA-1000 8 bit, 10 MHz digital oscilloscope. The signals from the endwall and sidewall transducers are depicted in Figs. 4 (a)-(c). A more detailed description of the procedure is given in Ref. [6].

The average of the velocity between the sidewall transducers and the velocity between the last sidewall transducer and the endwall is used as the shock wave velocity. The incident Mach number is determined from the initial sound speed. The Mach number and initial pressure and temperature of the driven section allow the final pressure and temperature to be calculated [5,6].

The ignition and burning of the particles is recorded with Motorola MRD500 semiconductor photo detector, which is sensitive in the wavelength region 0.35 to 1.25  $\mu\text{m}$ , with a peak sensitivity at 0.8  $\mu\text{m}$ . The particle radiation is collected with an 80 mm diameter aspheric collecting lens, reflected off a first-surface mirror, and is focused onto the photodiode. A typical photodiode signal is shown in Fig. 4 (d), and displays a three peak structure.

## Boron Particles

Two types of boron particles are used. The primary supply is a crystalline boron purchased from Aldrich Chemical Company, Inc., with a size range of 45  $\mu\text{m}$  or less and a quoted purity of 99%. For the tests to yield comparable results, the powder is sifted into specific size ranges with a Gilson vibrating shaker employing U.S. Standard sieves with mesh openings of 45, 38, 32, 25, and 20  $\mu\text{m}$  respectively. The stated tolerance of all mesh openings is  $\pm 3 \mu\text{m}$ .

Photographs of the particles (Fig. 5) were taken with a scanning electron microscope (SEM) which confirm the presence of larger crystalline particles with smaller ( $<1 \mu\text{m}$ ) parasitic particles stuck to the surface. The diameter of the larger particles is measured by the sedimentation technique with a Horiba CAPA-700 Particle Analyzer with glycerin as the dispersion fluid. Because the standard deviation is large and because measurements of many samples from the same size range resulted in a range of mean effective diameters, the particles are designated by the size of the sieve (e.g. 20  $\mu\text{m}$ ).

The second particle type is an amorphous boron purchased from the Johnson Matthey Catalog Company. Amorphous "particles" are actually agglomerates of smaller ( $<1 \mu\text{m}$ ) particles. An SEM photomicrograph shows that these particles range in size up to 7  $\mu\text{m}$ .

## Operating Conditions

Operating limits are determined from the structural design of the shock tube, which is rated for 100 atm. in the driver section. If oxygen is used, this corresponds to a test pressure of 34 atmospheres and a temperature around 3000 K [6]. Higher temperatures can be obtained if the desired test pressure is reduced below 34 atm. If other oxidizer gases are used, the test conditions change to account for the different molecular weights and different rates of dissociation. The initial ignition delay experiments with boron utilized 100 percent oxygen. The results from these tests were then used as the basis for comparison with experiments in which other gases were added to the oxygen.

The pure oxygen tests were used to indicate the boron particle size best suited for the experiments. Transient heating calculations were conducted to show that 45  $\mu\text{m}$  boron particles would ignite within one millisecond in gas temperatures of 3000 K. The size range available (20-25  $\mu\text{m}$ ) was therefore judged appropriate for a majority of the experiments. The initial experiments confirmed that 20  $\mu\text{m}$  particles ignited in less than one millisecond in a range of gas temperatures of 1900 to 3100 K.

Water vapor was the first oxidizer additive employed. Previous experiments [16] with boron and water vapor used water vapor mole fractions between 0.20 and 0.30, with the remaining gases consisting of a mixture of oxygen and carbon dioxide. The present research used 30% water vapor and 70% oxygen.

Sulfur hexafluoride was added to the oxygen in later experiments. A majority of these experiments were conducted with 1%  $\text{SF}_6$  added to 99% oxygen. Hydrogen fluoride was also tested, keeping the number of hydrogen fluoride molecules the same as the number of fluorine atoms in the sulfur hexafluoride experiments. Calculations show that dissociation of HF at the temperatures studied is less than one percent. HF/O<sub>2</sub> fractions of 6/94 and 12/88 percent were tested.

## EXPERIMENTAL RESULTS

Ignition delay and combustion time results for the shock tube experiments were determined as a function of temperature, pressure and particle size for each oxidizer mixture. The empirical measurement of these times is illustrated in Fig. 6, in which  $t_{\text{ign}}$  is defined as the numerical average of the times of three waveform features: base, half and peak, where  $t_H$  is the time at which the voltage is halfway between base and peak voltage. The extinction time,  $t_{\text{extinct}}$ , is found from the average of three times on the downward slope. The burning or combustion time is found by subtracting  $t_{\text{ign}}$  from  $t_{\text{extinct}}$ .

## Amorphous Boron

An investigation of amorphous boron ignition delay versus temperature for different pressures and oxidizers was conducted. The temperature range was 1400 to 2800 K. A typical broadband photodiode signal for amorphous boron is shown in Fig. 7, with time referenced to the shock arrival time at the endwall. All experiments with amorphous boron display a similar signal with a single voltage peak.

The nominal condition to which all results are compared (Fig. 8) is a reflected pressure of 8.5 atm. of a 100 percent oxygen atmosphere, showing an ignition limit of 1425 K. Use of 3% oxidizer  $\text{SF}_6$  reduces ignition delay time slightly from that for pure  $\text{O}_2$ .

## Crystalline Boron

As with the amorphous boron experiments, nominal conditions for crystalline boron are set at 8.5 atm with 100 % oxygen, using 20  $\mu\text{m}$  particles. The signal time history for 20  $\mu\text{m}$  crystalline boron (Fig. 9) is more complex than for amorphous boron particles (Fig. 7). For the oxygen experiments, most signals show three peaks and ignition delays are measured for all three. The first peak appears in all tests above 1800 K. It was originally thought that the first peak was due to the presence of parasitic particles on the crystalline particles (Fig. 5.), but this hypothesis was disproved by ignition tests at 3100 K and 8.5 atm using 1  $\mu\text{m}$  and 20  $\mu\text{m}$  crystalline boron particles and unsieved ( $<200 \mu\text{m}$ ) particles of  $\text{B}_2\text{O}_3$ . The first 100  $\mu\text{s}$  of the emission data from the tests are shown in Fig. 10, normalized in amplitude to the second peak, and display similar time histories for all three types of particles.

The smaller 1  $\mu\text{m}$  crystalline particles show the same behavior as the 20  $\mu\text{m}$  particles for the first two peaks, which tends to support the parasitic particle hypothesis. However, the  $\text{B}_2\text{O}_3$  particles also show the same behavior, and since  $\text{B}_2\text{O}_3$  particles do not have parasitic boron particles attached, it now seems more likely that the first two peaks are the result of oxide evaporation.

The second peak is not present in all cases. It appears consistently in the pure oxygen experiments, always attached to the first peak as shown. It also is present in a majority of the water vapor/oxygen experiments. However, in almost all of the  $\text{SF}_6/\text{O}_2$  tests, the second peak is non-existent.

Figure 11 depicts the ignition delay versus temperature trend for the first and second peaks at 8.5 atm. The 34 atm. data is similar and is not shown. The ignition temperature limit for the first two peaks is approximately 1900 K. There is a good deal of scatter in the first peak data and less for the second peak data. Data for both peaks shows a trend of decreasing delay time with increasing temperature. This would indicate the oxide layer removal rate increases with temperature, as would be expected.

Third peak ignition delay times for 20  $\mu\text{m}$  boron in 100%  $\text{O}_2$  at 8.5 and 34 atm. are shown in Fig. 12. The data display an ignition temperature limit of 1900 K, which is in agreement with other research [23]. There is a small pressure effect at temperatures below 2600 K and a decrease in ignition delay time with increasing temperature, with an average ignition delay time of about 250  $\mu\text{s}$  at 3000 K.

The burning time for 20  $\mu\text{m}$  boron particles is shown as a function of temperature in Fig. 13 at 8.5, 17 and 34 atm. The shortest burning time measured is 200  $\mu\text{s}$  while the longest approaches 1.0 ms. There is a great deal of scatter in this data and, similarly, for all other test conditions. Due to the high degree of scatter, burn time results are not mentioned further in this paper.

### **Water vapor and fluorine effects**

The main focus of this research was to determine if fluorine-containing compounds ( $\text{SF}_6$ , HF) affected the combustion history of boron particles. A set of experiments was also conducted with water vapor to confirm the results of previous work. Two different concentrations of each fluorine compound were investigated.

All of the experiments were conducted at a pressure of 8.5 or 34 atm. in an oxidizing atmosphere of oxygen plus  $\text{H}_2\text{O}$  or fluorine additive. The ignition delay time of the third peak is

shown in Figs. 14 through 17, where each oxidizer additive is compared to 100 percent oxygen to highlight specific results.

Figure 14 compares the third peak ignition delay of boron in water vapor/oxygen and pure oxygen. The ignition delay agrees at all temperatures to within the scatter of the data. No ignition is observed below 2100 K with water vapor and below 1900 K with oxygen.

Figure 15 displays the effect of  $\text{SF}_6$  at 8.5 atm. on third peak ignition delay. It was found that the addition of  $\text{SF}_6$  had no measurable effect on the delay for peak 1 at 8.5 or 34 atm., indicating that the oxide layer removal rate was not increased. It was found, however, that the second peak was seldom seen in  $\text{SF}_6$  experiments, which would suggest a change in the chemical pathway for the oxide removal reactions.

The addition of  $\text{SF}_6$  at 8.5 atm. (Fig. 15) has little effect on third peak ignition delay or on the ignition temperature limit. The limit for  $\text{SF}_6$  is 1900 K compared to 1900 K for the oxygen limit and 2200 K for the water vapor limit. When comparing data for 1%, 2%, and 3% mole fractions of  $\text{SF}_6$  (not shown here) there is little discernible difference.

Figure 16 shows data for 1%  $\text{SF}_6$  at 34 atm. There is a marked reduction in both ignition delay and ignition temperature limit for the  $\text{SF}_6$  data compared to the 100%  $\text{O}_2$  data. The ignition delay time is 200  $\mu\text{s}$  lower at 1900 K and is about 100  $\mu\text{s}$  lower at 2620 K. The ignition temperature limit for the  $\text{SF}_6$  data is around 1400 K compared to 1900 K for the pure oxygen data.

A side note on the  $\text{SF}_6$  experiments concerns the profile of the photodiode signal. At temperatures close to the ignition temperature limit for  $\text{SF}_6$ , the third peak was sharply defined, as compared to signals for pure  $\text{O}_2$  at temperatures close to its ignition temperature limit.

Figure 17 illustrates the ignition delay results from the hydrogen fluoride experiments. The ignition delay times are very similar to the oxygen case, but with no ignition observed below 2450 K. There does not appear to be a significant decrease ignition delay for HF with increasing temperature over the range studied. No difference in ignition delay was observed in tests conducted with 12% HF (data not shown).

## SUMMARY AND CONCLUSIONS

It was previously found elsewhere [16] that boron undergoes two-stage ignition. In the first stage particle combustion begins, but is retarded by the presence of a liquid oxide layer [2]. The first stage ends when there is a runaway of oxide evaporation, which removes energy and extinguishes the particle. In the second stage the particle re-ignites and burns to completion.

We also have observed two phase combustion, but have found that the first phase emission signal contains two peaks. From experiments conducted with 1  $\mu\text{m}$  crystalline boron and  $<200 \mu\text{m}$   $\text{B}_2\text{O}_3$  particles, we conclude that parasitic particles on the surface of the 20  $\mu\text{m}$  particles are not responsible for the two peak phenomenon. We instead suggest that removal of the boron oxide layer is responsible for both peaks.

Data from experiments in which  $\text{SF}_6$  was added show little decrease in ignition delay time at 8.5 atm., but a significant effect at 34 atm. There is also a decrease in the ignition temperature limit at 34 atm. from 1900 K to 1400 K compared to pure oxygen data. The addition of HF or  $\text{H}_2\text{O}$  in experiments did not produce any significant effect.

Based on the experimental measurements of boron ignition in pure oxygen, the following conclusions can be drawn:

- 1) Amorphous boron has an ignition limit of 1425 K at pressures above 8.5 atm., and ignition delay times decrease with increasing temperature from 40  $\mu\text{s}$  to an asymptotic value of 15  $\mu\text{s}$  at 2000 K. Higher pressures have negligible effects.
- 2) For 20  $\mu\text{m}$  crystalline particles, peaks 1 and 2 have a temperature ignition limit of 1900 K at pressures above 8.5 atm. The first and second peak ignition delay decreases with increasing temperature. Higher pressures do not affect the delay of either peak.
- 3) 20  $\mu\text{m}$  crystalline particles (peak 3) ignite in less than 1 ms at temperatures above 2500 K and approach an ignition delay time limit of 250  $\mu\text{s}$  at 3000 K for pressures above 8.5 atm. Increases in pressure show no measurable effects.

With additives, the results indicate the following:

- 1) Water vapor has no measurable effect on the ignition delay of 20  $\mu\text{m}$  crystalline boron at 8.5 atm. There is, however, a slight increase in the ignition temperature limit.
- 2) Sulfur hexafluoride reduces the ignition delay time of amorphous boron [1].  $\text{SF}_6$  (1% in  $\text{O}_2$ ) has little effect on the ignition delay time or the ignition temperature limit of 20  $\mu\text{m}$  particles at 8.5 atm., but at 34 atm., there is a reduction in ignition delay and a reduction in the ignition temperature limit to 1450 K. Using different percentages of  $\text{SF}_6$  does not affect the ignition delay. Therefore, it appears that fluorine atoms have a substantial effect on boron ignition at high pressures.
- 3) Hydrogen fluoride does not produce significant differences in ignition delay or burning time when compared to pure oxygen. Increasing the amount of HF does not change the results. Therefore, hydrogen fluoride does not observably enhance the chemical kinetics with boron or boron oxide, as predicted by other researchers [19].

### Continuing Research

In future experiments, it is desirable to search for reasons why hydrogen fluoride does not change the ignition delay times. One possible theory is that it is necessary to dissociate HF, which cannot be done at the relatively low temperatures in the shock tube. Future experiments to create HF *in situ* using water vapor and sulfur hexafluoride together might answer this question.

Further chemical kinetic modeling for combustion of boron in F/ $\text{O}_2$  atmospheres is required. It appears that fluorine not only assists in the combustion process, it appears to alleviate the long ignition delay at relatively low temperatures that has hindered the use of boron as a fuel.

### Acknowledgments

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## Figure Captions

Figure 1. Ignition model of boron particle showing various processes which occur during particle heating.

Figure 2. Conditions in a shock tube (a) initially, (b) after diaphragm is broken, and (c) after the shock wave reflects from the endwall.

Figure 3. Particle mounting technique and particle dispersal from incident and reflecting shock waves. Knife blade is located 8 mm from endwall. The window is quartz/polycarbonate composite, with the 6.35 mm thick quartz window in contact with the reflected shock.

Figure 4. Typical boron signals from (a) endwall pressure transducer, (b) first sidewall pressure transducer, (c) second sidewall pressure transducer, and (d) photodiode. The photodiode signal displays 3 peaks. All ignition times are referenced from  $t_{ew}$  in (a).

Figure 5. Photomicrograph of 20-25  $\mu\text{m}$  crystalline boron particles with attached sub-micron parasitic particles, at 300x magnification. White micron bar length is 100  $\mu\text{m}$ .

Figure 6. Boron emission signal at 3100 K illustrating definitions for ignition and extinction time.

Figure 7. Typical amorphous ( $\sim 1 \mu\text{m}$ ) boron emission signal in pure oxygen showing the characteristic single voltage peak.

Figure 8. Amorphous boron ignition delay versus temperature for two oxidizers at a nominal pressure of 8.5 atm.

Figure 9. Typical crystalline boron emission signal at 2560 K showing the characteristic three peak signal.

Figure 10. First 100  $\mu$ s of emission data from amorphous boron oxide and crystalline boron particles. Data is normalized to the second peak for each experiment shown.

Figure 11. Ignition delay time versus temperature of the first and second peaks in 100% oxygen atmosphere at 8.5 atm. for a 20  $\mu$ m crystalline boron particle sample.

Figure 12. Third peak ignition delay time versus temperature in 100% oxygen atmosphere at 8.5 and 34 atm. for 20  $\mu$ m crystalline boron particles.

Figure 13. Burning time versus temperature of the third peak in 100% oxygen atmosphere for 20  $\mu$ m crystalline boron particles at pressures of 8.5, 17, and 34 atm.

Figure 14. Third peak ignition delay time versus temperature, comparing water vapor and oxygen for 20  $\mu$ m boron particles at 8.5 atm.

Figure 15. Ignition delay time versus temperature of the third peak comparing SF<sub>6</sub> and O<sub>2</sub> for 20  $\mu$ m boron particles at 8.5 atm.

Figure 16. Ignition delay time versus temperature of the third peak comparing SF<sub>6</sub> and O<sub>2</sub> for 20  $\mu$ m boron particles at 34 atm.

Figure 17. Ignition delay time versus temperature comparing 6 % HF and O<sub>2</sub> for 20  $\mu$ m boron particles at 8.5 atm.

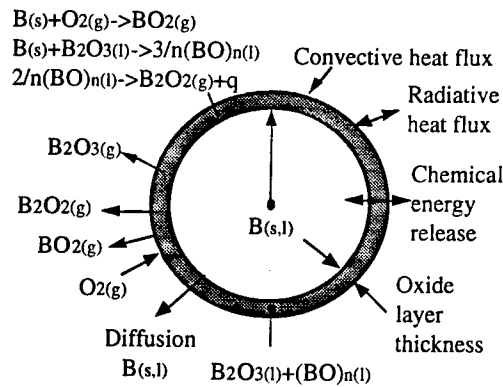


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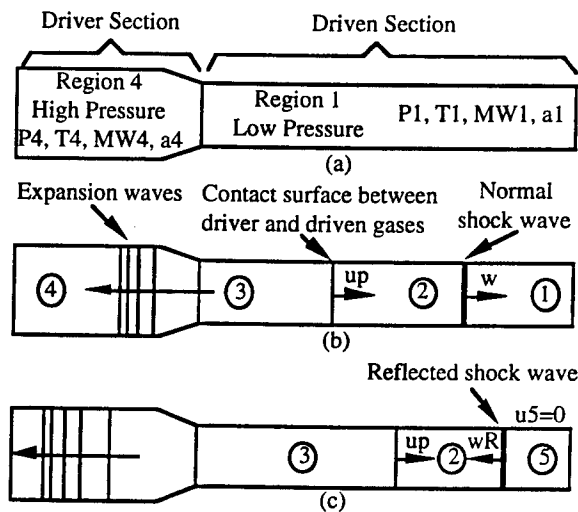


Figure 2. Conditions in a shock tube (a) initially, (b) after diaphragm is broken, and (c) after the shock wave reflects from the endwall.

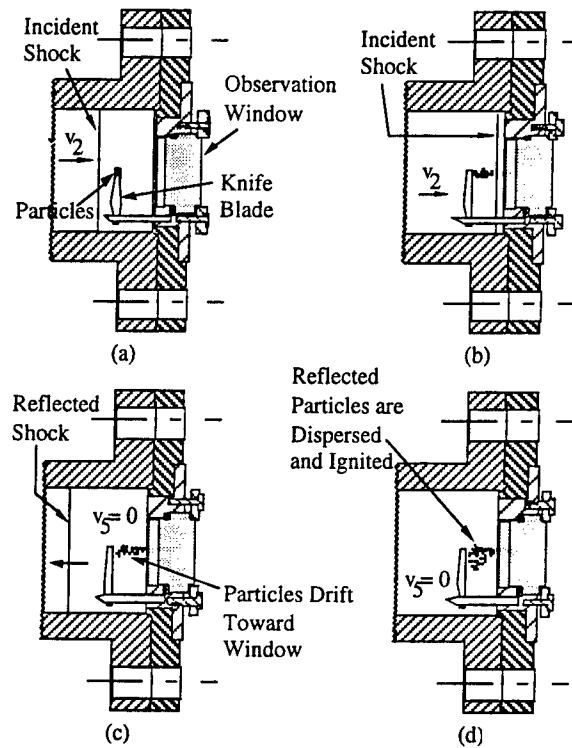
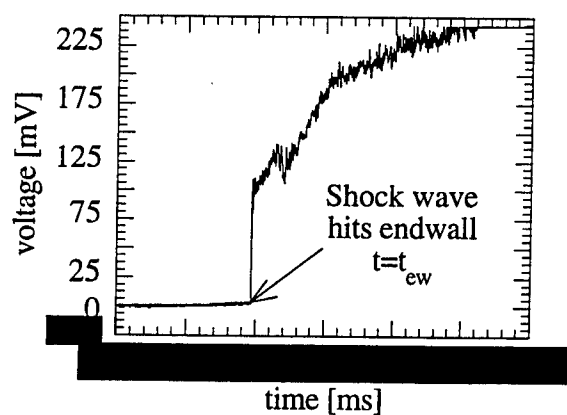
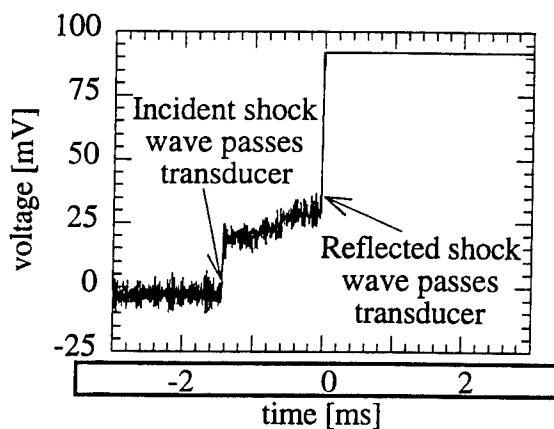


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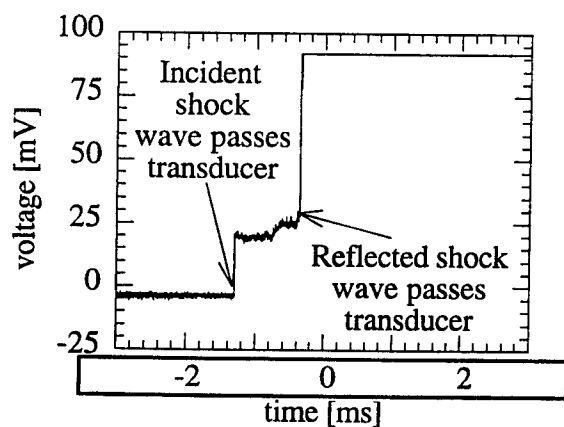




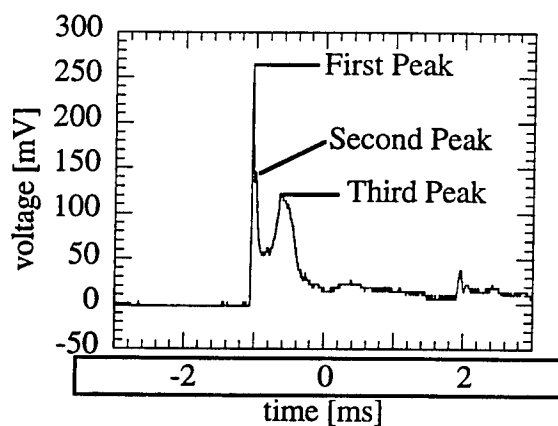
(a)



(b)



(c)



(d)

Figure 4. Typical boron signals from (a) endwall pressure transducer, (b) first sidewall pressure transducer, (c) second sidewall pressure transducer, and (d) photodiode. The photodiode signal displays 3 peaks. All ignition times are referenced from  $t_{ew}$  in (a).

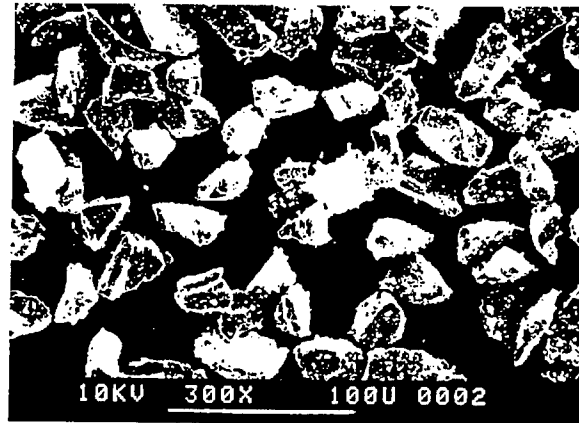


Figure 5. Photomicrograph of 20-25  $\mu\text{m}$  crystalline boron particles with attached sub-micron parasitic particles, at 300x magnification. White micron bar length is 100  $\mu\text{m}$ .

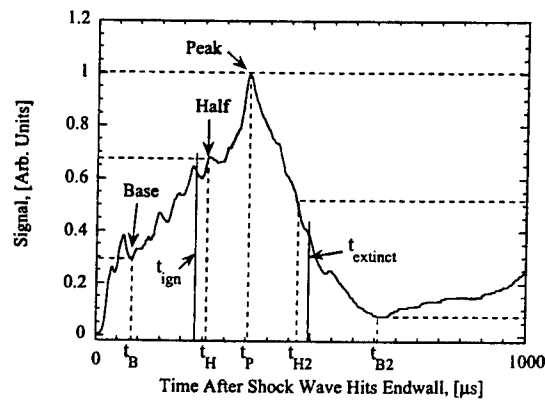


Figure 6. Boron emission signal at 3100 K illustrating definitions for ignition and extinction time.

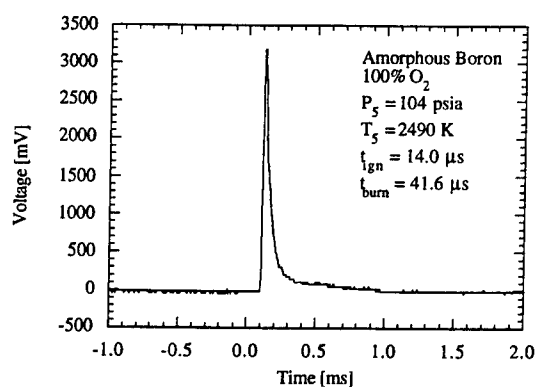


Figure 7. Typical amorphous ( $\sim 1 \mu\text{m}$ ) boron emission signal in pure oxygen showing the characteristic single voltage peak.

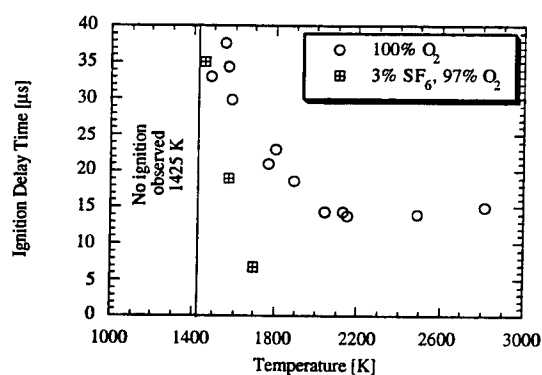


Figure 8. Amorphous boron ignition delay versus temperature for two oxidizers at a nominal pressure of 8.5 atm.

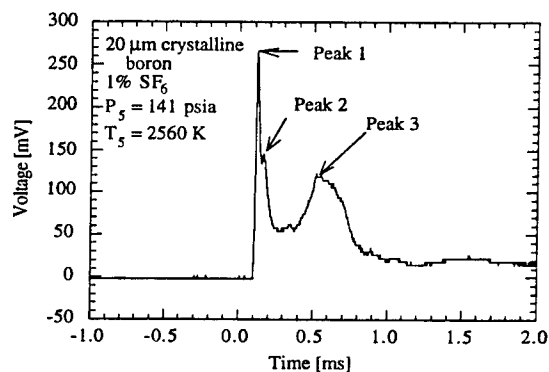


Figure 9. Typical crystalline boron emission signal at 2560 K showing the characteristic three peak signal.

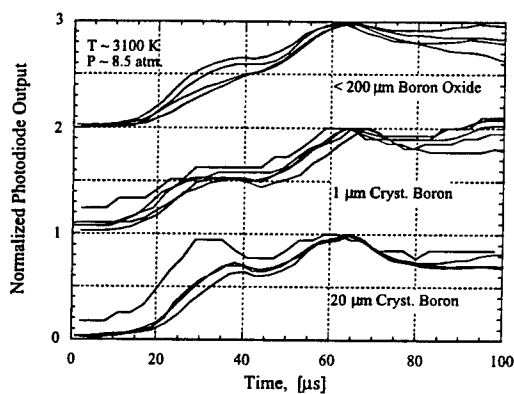


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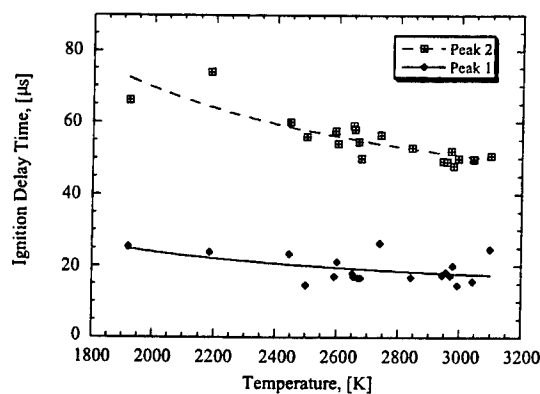


Figure 11. Ignition delay time versus temperature of the first and second peaks in 100% oxygen atmosphere at 8.5 atm. for a 20 μm crystalline boron particle sample.

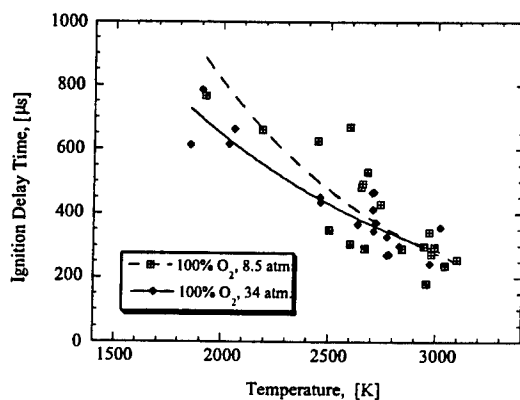


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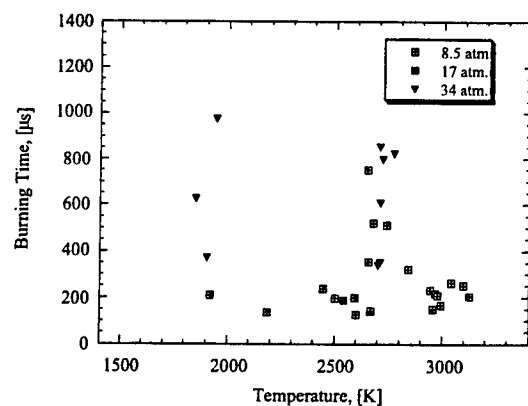


Figure 13. Burning time versus temperature of the third peak in 100% oxygen atmosphere for 20  $\mu\text{m}$  crystalline boron particles at pressures of 8.5, 17, and 34 atm.

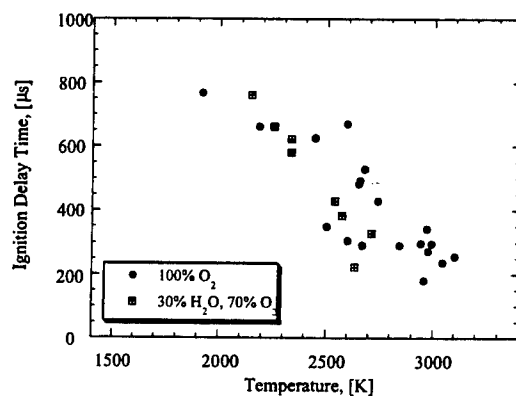


Figure 14. Third peak ignition delay time versus temperature, comparing water vapor and oxygen for 20  $\mu\text{m}$  boron particles at 8.5 atm.

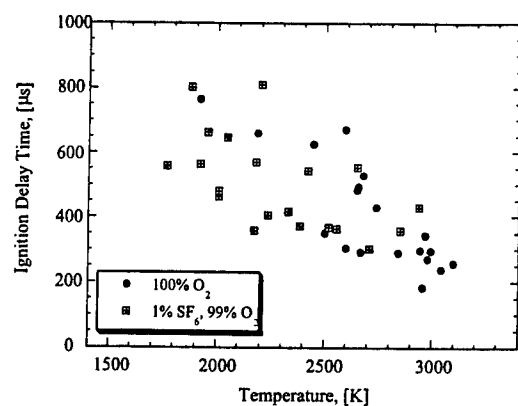


Figure 15. Ignition delay time versus temperature of the third peak comparing SF<sub>6</sub> and O<sub>2</sub> for 20 μm boron particles at 8.5 atm.

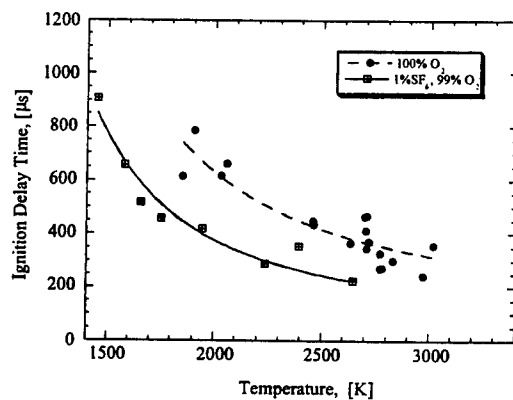


Figure 16. Ignition delay time versus temperature of the third peak comparing SF<sub>6</sub> and O<sub>2</sub> for 20 μm boron particles at 34 atm.

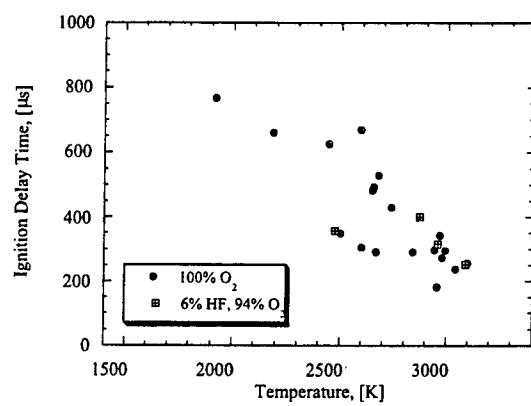


Figure 17. Ignition delay time versus temperature comparing 6 % HF and O<sub>2</sub> for 20 μm boron particles at 8.5 atm.



## SECTION III

### HIGH PRESSURE IGNITION OF BORON IN REDUCED OXYGEN ATMOSPHERES

R.O. FOELSCH, M.J. SPALDING, R.L. BURTON, H. KRIER

*[This section is material published in the MRS Symposium Proceedings Series, T. B. Brill, T. P. Russell, W. C. Tao, R. B. Wardle, eds., Vol. 418, pp. 187-193, 1996.]*

#### ABSTRACT

Boron ignition delay times for 24  $\mu\text{m}$  diameter particles have been measured behind the reflected shock at a shock tube endwall in reduced oxygen atmospheres and in a combustion bomb at higher pressures in the products of a hydrogen/oxygen/nitrogen reaction. The shock tube study independently varies temperature (1400 - 3200 K), pressure (8.5, 34 atm), and ignition-enhancer additives (water vapor, fluorine compounds). A combustion chamber is used at a peak pressure of 157 atm and temperature in excess of 2800 K to study ignition delays at higher pressures than are possible in the shock tube.

#### INTRODUCTION

Boron has been considered for many years as a prime candidate for high enthalpy fuel formulations, as an additive to solid propellant formulations, and as an additive for tailoring the energy release within explosive grains. Theoretically, boron shows great promise based on the high potential energy release both on a volumetric and gravimetric basis. The high enthalpy of combustion, high combustion temperature, and low molecular weight products also suggests a promising application in rocket propellants.

In practice the energy potential of boron additives in propellant formulations has been difficult to harness. Ignition is hindered by a protective oxide coating which is continually replenished by exothermic reactions until it can be removed from the particle surface. Boron combustion is made difficult by the high vaporization temperature ( $T_v = 4100$  K at 1 atm) of boron which limits oxidation to slower heterogeneous surface reactions. Condensation of the product species ( $\text{B}_2\text{O}_3$ ) is also a slow process which must occur at relatively low temperatures, and in the presence of hydrogenated species the product routes change in favor of gas phase species ( $\text{HBO}_2$ ), reducing additional energy release from condensation.

Several theoretical studies [1,2] and more recent experimental findings [3-6] have warranted the examination of oxide layer removal-enhancing agents. Hydrogenated and fluorinated compounds show promise and many of these compounds already exist in typical propellant formulations. Experimental results from Macek [7] and Krier, et al. [3] indicate that operation at elevated pressures also improves boron particle ignition.

Macek and Semple [8] experimentally found reduced boron ignition times for wet flat-flames compared to dry flames over a range of temperatures below 2900 K at 1 atm pressure. More recently, Krier, et al. [3] have provided further evidence of the ignition-enhancing effects of water vapor and fluorine at higher pressures. Results from shock-initiated combustion of 24  $\mu\text{m}$  boron particles indicate that water vapor (30%) in oxygen marginally reduces delays at ambient temperatures above 2600 K at 8.5 atm, whereas traces of fluorine (obtained by dissociating sulfur

hexafluoride, SF<sub>6</sub>, 1 and 3%) in oxygen significantly reduce ignition delay times between 1400 and 2700 K at 8.5 and 34 atm, when compared to pure oxygen alone. Hydrogen fluoride (HF, 6 and 12%) added to oxygen did not produce any beneficial decrease in ignition delay times between 2500 and 3100 K at 8.5 atm, suggesting that free fluorine atoms are likely the active agent, and not necessarily fluorine compounds as suggested earlier [9].

In this paper we introduce newer measurements of boron ignition delays in reduced oxygen atmospheres. Particle data are obtained behind reflected shock waves at 34 atm and at higher pressures in nitrogen diluted hydrogen/oxygen mixtures in a combustion bomb. We compare these newer data to previous determinations at lower pressures.

## EXPERIMENTS

Shock-initiated particle combustion experiments are conducted behind the reflected shock wave in the endwall region of a 12 meter long, double diaphragm, cylindrical cross-section stainless steel shock tube, fully described elsewhere [3,10]. The driven section is 8.4 m long by 8.9 cm in diameter and is coupled to a 3.3 m long, 16.5 cm diameter driver section by a converging nozzle and diaphragm section. Optical access to the near-endwall region is obtained axially through the endwall by focusing optics. Test temperature, pressure, and composition of the oxidizing environment are independently varied to cover a wide range of operating conditions. Particles are mounted on a hobby knife blade and are swept off by the incident shock wave to be ignited in the hot, stagnated gases behind the reflecting shock [10].

The high pressure combustion chamber is a megajoule-class combustion bomb designed for transient pressures to 3400 atm and transient temperatures to 4000 K. The 66 cm high by 51 cm diameter vessel is fabricated from heat-treated 4340 carbon-steel. The vessel is capped by a 25 cm diameter plug which closes the central 2.0 liter cylindrical chamber cavity. For these experiments, a chamber insert has been used to give an effective 1.0 liter volume. All diagnostics are mounted in the plug, consisting of both static and dynamic pressure measurements, inlet gas temperature, and centerline-viewing optical emission detection through a high pressure optical window. Ignition of the gas mixture is achieved by an electrical discharge through a foil-type igniter which produces an intense spark at the anode/foil point of contact, even at high initial

pressure. Particles are mounted in a recess on the tip of a cone situated 2 cm below the optical window, and are dispersed by the advancing combustion front. Calculations show that the particles do not reside in the cone's thermal layer nor are they dispersed beyond the optical field of view.

Several important characteristic timescales for both experiments are listed and compared in Table I. The fast-rising pressure and temperature profile of the reflected shock wave is ideal for particle

**Table I :** Characteristic times for shock tube and combustion chamber experiments.

Characteristic Times, [ $\mu$ sec]	Shock Tube	Combustion Chamber
Pressure Rise	< 1 <sup>a</sup>	640 <sup>b</sup>
Temperature Rise	< 1 <sup>a</sup>	10 <sup>c</sup>
Total Test	500-1000 <sup>d</sup>	3000 <sup>d</sup>
Heat Loss	5000 <sup>e</sup>	5000 <sup>e</sup>
Wall Thermal Layer Growth	50 <sup>e</sup>	50 <sup>e</sup>

<sup>a</sup> across reflected shock.

<sup>d</sup> within 10% of peak.

<sup>b</sup> of entire chamber.

<sup>e</sup> predominantly radiation.

<sup>c</sup> across deflagration front.

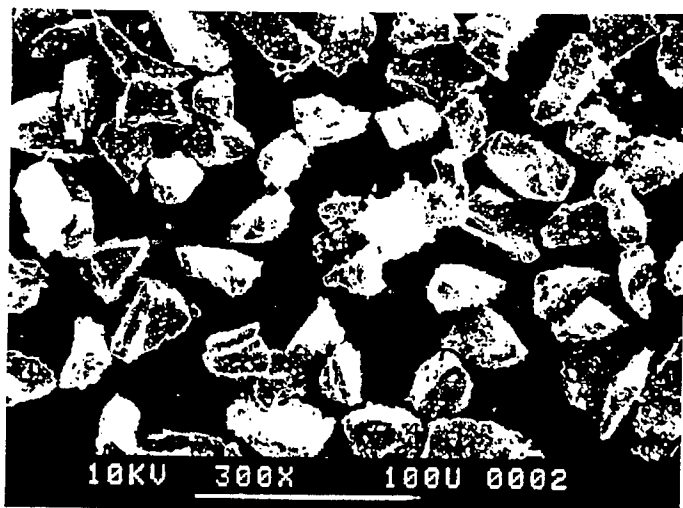


Fig. 1 : Photomicrograph of 24  $\mu\text{m}$  crystalline boron particles with attached sub-micron parasitic particles, at 300x magnification. White micron bar length is 100  $\mu\text{m}$ .

are achieved for several milliseconds after peak pressure is established.

Crystalline boron particles were obtained by sieving raw samples from Aldrich Chemical Co. (purity 99.0%) and Goodfellow, Corp. (purity 99.6%). The separate batches showed similar particle sizing and ignition characteristics. Statistical sizing analysis gives an effective mean diameter of  $23.9 \pm 3.9 \mu\text{m}$ , determined by sedimentation technique [11]. A sample photomicrograph of the powder (Fig. 1) shows sub- $\mu\text{m}$  sized parasitic particles clinging to the surface after sieving. Higher magnification exposures suggest that many of the smaller particles may be fused to the large particle surface. Smaller  $\sim 1 \mu\text{m}$  crystalline boron and unsieved amorphous boron oxide ( $\text{B}_2\text{O}_3$ ) were obtained respectively from the Naval Research Laboratory [12] (purity 99.5%) and Aldrich Chemical Co. (purity 99.98%). The unsieved boron oxide particles range in size from sub- $\mu\text{m}$  to greater than 100  $\mu\text{m}$ .

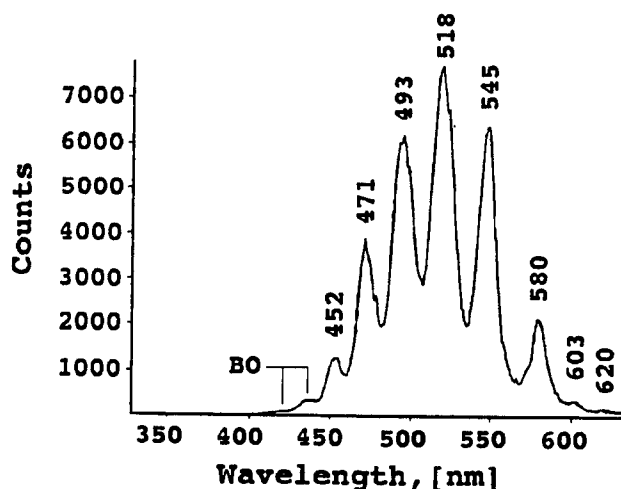


Fig. 2 : OMA spectrum of  $\sim 1 \mu\text{m}$  crystalline boron particles in pure oxygen showing characteristic  $\text{BO}_2$  bands.  $\text{BO}$  bands at 422.8 and 436.3 nm are also detectable. Data obtained in shock tube at 8.5 atm, 3100 K with 200  $\mu\text{sec}$  exposure.

ignition studies, although tests in our shock tube are limited to 34 atm and 3200 K by driver-section design considerations. The combustion chamber employs hydrogen/oxygen mixtures diluted with considerable nitrogen to avoid detonation. The rise time to ambient conditions is limited by flame front propagation through the chamber, and the pressure rise time is even longer, since the gases are free to expand in front of the advancing flame front. The temperature wave is localized, and peak temperature is achieved immediately behind the flame front. Constant pressure conditions

## SHOCK TUBE AND COMBUSTION CHAMBER RESULTS

Particle combustion time histories are measured indirectly by monitoring combustion emissions in the broadband and at selected wavelengths. Optical bandpass filters are selectively employed to monitor two reactive intermediary gas-phase species, the  $\text{BO}_2$  molecule about the 545 nm band and  $\text{BO}$  about its 436 nm band [13]. These species are expected to form throughout the combustion event. This choice is supported by the experience of others [4,6] and our own

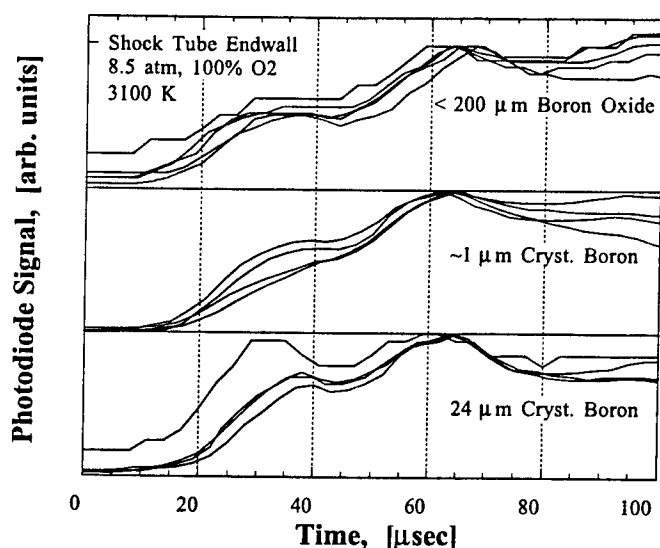


Fig. 3 : Normalized emission of amorphous boron oxide ( $B_2O_3$ ) and crystalline boron particles detected by photodiode filtered at  $546.1 \pm 5$  nm.

signal is obtained by subtracting out the background emission signal, which then shows the net boron signal returning to zero after  $\sim 2$  msec (see Fig. 5).

Ignition is assumed to occur at the half-maximum point in the filtered photodiode output signal. Ignition delay time is defined in practice as the time from the temperature stimulus (reflected shock, combustion front) to the point of ignition, and the combustion (burn) time as the time from ignition to the time when the filtered photodiode output signal has fallen back to half-maximum [3,10]. For combustion chamber experiments, ignition and burn times are obtained from the net boron signal. Work to be reported [14] will include detailed data for the burn time of boron particles at these conditions.

Previous results in the shock tube for boron particle ignition [3] in pure oxygen reveal ignition delays ( $t_{ign}$ ) which are a strong function of temperature below 2400 K for pressures of 8.5 and 34 atm and which asymptote to  $\sim 300$   $\mu$ sec at higher temperature for both pressures. The high pressure data can be expressed as a function of temperature by an equation of the form:

$$t_{ign} = A_0 \exp(E_0/T) \quad (1)$$

where  $A_0$  and  $E_0$  are empirically fit constants. In pure oxygen at 34 atm  $A_0 = 80$   $\mu$ sec and  $E_0 = 4100$  K between 1850 and 3000 K. With 1%  $SF_6$  additive to oxygen at 34 atm,  $A_0 = 44$   $\mu$ sec and  $E_0 = 4300$  K between 1450 and 2650 K. For 30%  $H_2O$  in oxygen at 8.5 atm,  $A_0 = 8.3$   $\mu$ sec and  $E_0 = 9800$  K between 2150 and 2700 K. Ignition delays in pure oxygen are slightly reduced below 2400 K as pressure is increased from 8.5 to 34 atm, while delays with traces of fluorine are significantly reduced as pressure is increased.

spectral analysis obtained with a gateable optical multichannel analyzer (OMA). A sample shock tube spectrum obtained over a 200  $\mu$ sec exposure initiated at the time of shock reflection from the endwall at 8.5 atm in pure oxygen burning  $\sim 1$   $\mu$ m crystalline boron is shown in Fig. 2.

Bandpass-filtered photodiode output as shown in Figs. 3 and 4 is analyzed to determine particle ignition and burn times for the shock tube. Photodiode traces in the combustion chamber have similar characteristics to the shock tube, but display hot background gas emission at long times. The net combusting boron particle

Recent experiments in oxidizing mixtures of O<sub>2</sub> in Ar and O<sub>2</sub> + 1% SF<sub>6</sub> in Ar were performed at  $34.3 \pm 1.9$  atm pressure and  $2950 \pm 87$  K. Oxygen mole fractions were varied from 100% to 5%. The ignition delay times follow a relationship of the form:

$$t_{ign} = C_0 \exp(-D_0 X_{O_2}) \quad (2)$$

where  $C_0$  and  $D_0$  are empirical constants and  $X_{O_2}$  is the mole fraction of oxygen. For O<sub>2</sub> in Ar, the constant  $C_0 = 840 \mu\text{sec}$  and  $D_0 = 1.0$ . For O<sub>2</sub> + 1% SF<sub>6</sub> in Ar,  $C_0 = 510 \mu\text{sec}$ ,  $D_0$

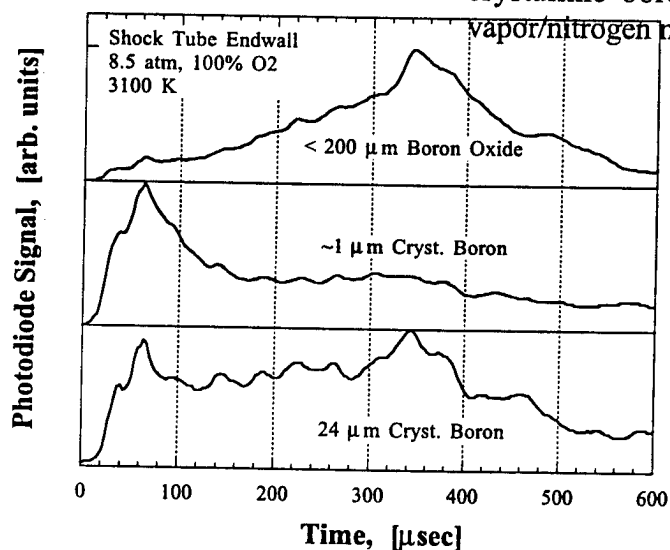


Fig. 4 : Amorphous boron oxide (B<sub>2</sub>O<sub>3</sub>) and crystalline boron particle emission detected by photodiode filtered at  $546.1 \pm 5$  nm.

34% H<sub>2</sub>O, 2% OH, 2% NO, and 51% N<sub>2</sub> and attain 2876 K with negligible decrease during the test time due to heat loss (Table I).

## DISCUSSION

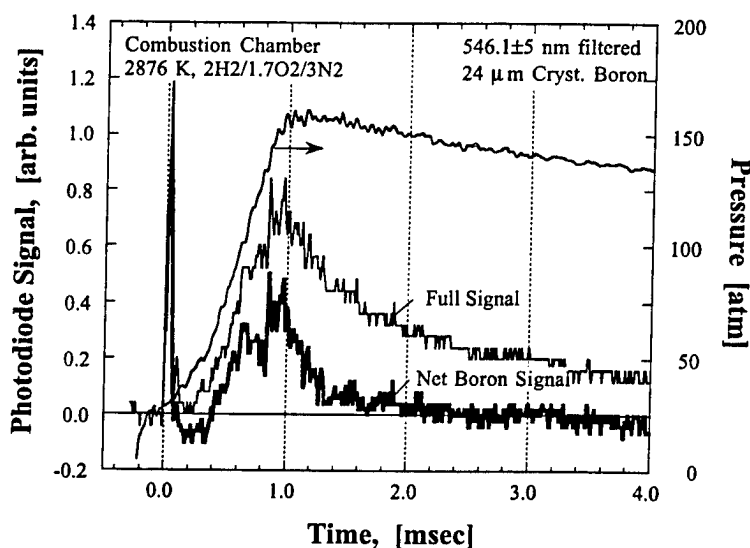


Fig. 5 : Filtered photodiode signal ( $546.1 \pm 5$  nm) measurement showing full and net emission signals from  $24 \mu\text{m}$  crystalline boron particles igniting in oxygen/water vapor/nitrogen mixture, in combustion chamber.

= 0.5. Thus ignition delays roughly increase a factor of 2.5 for pure oxygen and a factor of 1.5 with fluorine present, when oxygen mole fractions are reduced to 5%.

Ignition delay times are measured for  $24 \mu\text{m}$  crystalline boron particles igniting in the reaction products of a 2.0 mole hydrogen/1.7 mole oxygen/3.0 mole nitrogen mixture. Data (Fig. 6) indicate the ignition delay time is  $390 \pm 100 \mu\text{sec}$ . Peak combustion pressure is 157 atm, but particle ignition occurs while pressures are still rising in the chamber, typically at one-third of peak pressure. Equilibrium calculations predict the reaction products are composed of 11% O<sub>2</sub>,

Measured ignition delays in the combustion chamber at ~52 atm is similar to reduced-oxygen shock tube data in Fig.6 but is longer than shock tube data described by Eq. (1) at 8.5 atm when water vapor is present. Figure 6 also shows atmospheric pressure ignition delay data from Macek and Semple [8] using 34.6  $\mu\text{m}$  particles. The Macek data show an order-of-magnitude longer ignition delay, which we ascribe to the effect of pressure.

Our analysis of experimental data [11] on pressure effects indicates a small decrease in ignition delay in pure oxygen for a pressure increase from 8.5 to 34 atm, between 1900 and 2400 K, and no decrease above 2400 K. The recent modeling work of Yeh and Kuo [15] at 1800K predicts a 3-fold decrease in ignition delay in a reduced oxygen/water vapor mixture when pressure is increased from 1 to 8.5 atm total pressure. Their model predicts an additional 25% decrease in delay when pressure is increased from 8.5 to 34 atm, showing a similar trend to our pure oxygen experiments. Additional delays may also be caused by finite particle heating times experienced in the Macek experiments. The difference in particle size is negligible based on numerous experimental determinations [4,7,11].

We observe a multiple-stage ignition and combustion process for crystalline boron. Bandpass-filtered emission signals ( $546.1 \pm 5$  nm) for three distinct types of particles are compared in Figs. 3 and 4 from identical shock tube experiments at 8.5 atm and 3100 K. In Fig.3 we compare the first 100  $\mu\text{sec}$  of the normalized photodiode output for 24  $\mu\text{m}$  crystalline boron, ~1  $\mu\text{m}$  crystalline boron, and unsieved amorphous boron oxide ( $\text{B}_2\text{O}_3$ ) powder. Figure 4 shows the entire emission signal for these same experiments out to 600  $\mu\text{sec}$ .

Three local maxima are observed in the photodiode outputs for each of the three types of powders. The first two local maxima occur at 35  $\mu\text{sec}$  and 65  $\mu\text{sec}$ , displaying the same signature irrespective of particle size and composition. Since all three powders exhibit similar time histories up to 100  $\mu\text{sec}$ , we believe that the thin (10-100Å) boron oxide layer is being removed in all three cases, leading to gaseous  $\text{BO}_2$ . The oxide layer thickness is postulated from boron combustion models [1,4,15].

We identify the first two peaks as the first combustion stage, defined in the literature as the oxide layer removal stage. Figure 4 shows that the oxide layer is substantially removed over the first 100  $\mu\text{sec}$ . This suggests a lower limit for ignition delay time of 100  $\mu\text{sec}$  in pure oxygen at 3100 K, 8.5 atm and indicates that the use of boron particles of any size requires significant ignition-enhancement to achieve a sub-100  $\mu\text{sec}$  ignition delay. In Fig. 4 a third local maximum at ~350  $\mu\text{sec}$  is shown for

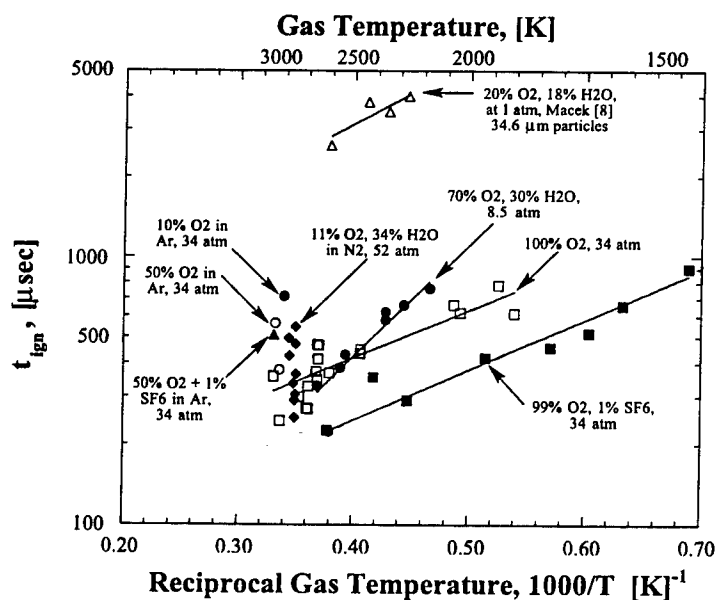


Fig. 6 : Ignition delay time for 24  $\mu\text{m}$  crystalline boron particles at high pressure and various oxidizers. Flat-flame burner data [8] used 34.6  $\mu\text{m}$  particles at 1 atm.

B<sub>2</sub>O<sub>3</sub> and 24  $\mu$ m boron particles. We attribute the third maximum for 24  $\mu$ m boron to full-fledged particle combustion; i.e., the second stage combustion of the oxide-free boron particle. The third peak for B<sub>2</sub>O<sub>3</sub> is presumable due to the emission signal of dissociating oxide from the larger (< 200  $\mu$ m) boron oxide particles. For  $\sim$ 1  $\mu$ m boron particles the first and second combustion stages are indistinguishable.

## SUMMARY AND CONCLUSIONS

In our experiments the boron particles are exposed to high temperature and high pressure which quickly melt the particle and its oxide shell. The oxide removal is then controlled by vaporization ( $T_v = 2450$  K) and surface chemistry processes [1,15]. During ignition, and later during combustion, the sub-oxides BO, BO<sub>2</sub>, and HBO in hydrogenated mixtures, are liberated at the liquid-gas interface.

Ignition-enhancing agents which reduce particle ignition delays are believed to assist actively in the gasification of the oxide layer. Reactive species including H<sub>2</sub>O, OH, H, F, and boron sub-oxides (BO, BO<sub>2</sub>) are absorbed at the liquid oxide-layer surface and chemidesorb gas phase species after causing chemical bond rearrangement. Cluster beam experiments [5] indicate that H<sub>2</sub>O and HF have greater reaction probabilities than oxygen. Our observations of ignition delays indicate that enhancement occurs marginally with H<sub>2</sub>O above 2600 K, and does not occur significantly with HF.

In summary, the data indicate that boron particles at high pressure experience an oxide removal stage lasting  $\sim$ 100  $\mu$ sec at 3100 K, that the high pressure (8.5-52 atm) reduces ignition delay by an order-of-magnitude compared to 1 atm, that the reduction in O<sub>2</sub> mole fraction to 5% increases ignition delay by a factor of  $\sim$ 2 near 3000 K, and that SF<sub>6</sub> exhibits significant ignition enhancement.

## ACKNOWLEDGMENTS

The authors would like to thank the many contributions of S. Pirman, R. McMullen, C. Meyers, and D. Schneider for help in execution of the experiments, and the expert work of P. Hetman, D. Roberts, and R. Coverdill during fabrication of the combustion chamber facility and their continued expert advice. We are grateful for the many helpful comments of J. Black during the design of the combustion chamber. The authors acknowledge the sponsorship of the Office of Naval Research, Grant Nos. N00014-93-1-0654 and -1206. Dr. R. Miller is the Project Director.

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## Appendix

### AASERT Student Progress Report

for the period August 21, 1995 - August 20, 1996

#### A. Robert O. Foelsche

Mr. Foelsche's grades are excellent. He has a 4.9 out of 5.0 grade point average.

His research progress is excellent. After completing the fabrication and assembly of a high pressure combustion bomb for boron combustion studies, the first shot was taken in September, 1994. The 1.5 liter bomb has a peak design pressure of 50,000 psi (3400 atm), and can be charged with a hydrogen-oxygen helium mixture to an initial pressure of 3000 psi. Mr. Foelsche has designed and supervised fabrication of all auxiliary systems including control, charging and exhaust tank systems, spark igniter, fiber optic window for photodiode and OMA studies, and piezoelectric pressure probe. He is currently conducting an investigation of the ignition and burn times of amorphous boron, 20  $\mu\text{m}$  crystalline boron and of 100  $\mu\text{m}$  filamentary boron. He attended the workshop on boron combustion held at Pennsylvania State University in June, 1995, where his results were presented by the University of Illinois research team.

Mr. Foelsche is continuously reviewing the boron combustion literature, and has performed chemical kinetics calculations for mixtures of interest. It is anticipated that his thesis will be completed by December, 1996, and that he will graduate shortly thereafter. He is currently considering a two-year post-doctoral position at NSWC -- China Lake.

#### B. Martin Spalding

Mr. Spalding began his research supported by this AASERT on August 21, 1994, working first on his MSE degree with a likelihood of continuing towards his Ph. D. degree after completing his Master's requirement in September, 1996. Mr. Spalding is responsible for the experiments dealing with emission spectroscopy of boron oxides during boron powder ignition in a high pressure shock tube. He is continuing the previous research of Mr. Steve Pirman (past AASERT-supported grad student) and co-authored a paper with Pirman, H. Krier and R. L. Burton, which appeared in the July-August, 1996 issue of the AIAA Journal of Propulsion and Power.

Mr. Spalding is responsible for emission spectroscopy during the ignition events, measuring spectra for BO and BO<sub>2</sub>. Measurements of B<sub>2</sub>O<sub>3</sub> using a gated OMA system and an infrared optical detector are being done with graduate student Thomas Rood. That work requires spectral resolution measurements accurate in periods of 0.5 milliseconds or less.

His academic performance is very good; he received grades of four A's and two B's in six graduate courses in his first three semesters.